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per Col. Lindsay of ARPA X 79073 Egan  
6/4/63 mhc.

# I. PURPOSE

Our primary objective is to broaden the linewidth of ruby without disturbing its optical quality significantly, by placing  $\text{Cr}^{3+}$  in dilute solid solutions of  $\text{Al}_2\text{O}_3$  and  $\text{Ga}_2\text{O}_3$  and/or  $\text{Al}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ . Since the fluorescent transition in ruby is so strongly dependent on crystal field, a very modest impurity concentration should be sufficient to broaden the linewidth. We plan to grow a two inch long, very narrow linewidth, low strain ruby by growth from a molten salt. Then, we plan to grow by the same method crystals of  $\text{Al}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  activated with  $\text{Cr}^{3+}$ . This should give us broad linewidth  $\text{Cr}^{3+}$  fluorescence with little or no change in the optical quality of the host crystal.

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II. ABSTRACT

Ruby crystals <sup>were</sup> ~~have been~~ grown from molten salt solutions consisting of mixtures of  $PbO$  and  $PbF_2$ . Using a similar method, Ga doped ruby crystals <sup>were</sup> ~~have been~~ grown. Analytical procedures for the detection of Ga in the presence of ruby <sup>were</sup> ~~have been~~ developed.

Several important factors in the growth of both doped and undoped ruby crystals <sup>were</sup> ~~have been~~ found to be sensitive to the  $PbF_2$  content. Some of these factors are:  $Al_2O_3$  solubility, crystal habit, crystal quality, and dopant concentration. A mechanism for the growth of ruby from  $PbO$ - $PbF_2$  fluxes is proposed.

Equipment for the handling of large melts <sup>was</sup> ~~has been~~ designed. Apparatus for linewidth measurements <sup>was</sup> ~~has been~~ completed.

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#### IV. INTRODUCTION

Our objective is to broaden the linewidth of ruby without disturbing its optical quality significantly, by placing  $\text{Cr}^{3+}$  in dilute solid solutions of  $\text{Ga}_2\text{O}_3$  and/or  $\text{Y}_2\text{O}_3$  in  $\text{Al}_2\text{O}_3$ . Since the fluorescent transition in  $\text{Cr}^{3+}$  is so strongly dependent on the crystal field, a very modest impurity concentration should be sufficient to broaden the linewidth. We plan to grow a two inch long, very narrow linewidth, low strain ruby from a molten salt solution. Then, using a similar method, we plan to grow crystals of  $\text{Al}_2\text{O}_3$ - $\text{Ga}_2\text{O}_3$  or, if necessary,  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$  activated with  $\text{Cr}^{3+}$ . This should give us broad linewidth  $\text{Cr}^{3+}$  fluorescence with little or no change in the optical quality of the host crystal.

It is the feeling of the Airtron technical staff that meaningful progress in the growth of crystals cannot be achieved from haphazard experiments performed in underdesigned and incompletely engineered equipment. A better understanding of the phase equilibria and kinetics of the system can be obtained only by performing systematic experiments under carefully controlled and reproducible conditions. The development of reliable analytical techniques is also a prerequisite to the solution of this problem.

Molten salt crystal growth runs made early in the contract period, suggested that two major problems had to be solved before the contract goal could be achieved. First, the controlled growth of doped and undoped ruby crystals requires at least a partial understanding of the phase equilibria and crystallization kinetics of the system. Many small runs must be made before large crystals possessing predictable characteristics can be grown. Second,

Introduction (Continued)

in common with all previous molten salt systems investigated, the largest and best crystals grow from the largest melts. Therefore, the problem of handling large masses of molten material has to be solved. The system described is the largest known to exist anywhere in the world at the present time.

The solution of these two problems was undertaken simultaneously.

V. STATUS

A number of goals for this report period were established in the previous report. Table I shows the current status of these goals together with estimated completion dates.

While our progress with respect to meeting the above objective has been good, several unanticipated problems arose which prevented attainment of even more goals. These were:

1. Equipment acquisition required at least twice as much time as predicted.
2. Equipment installation was delayed by the concurrent consolidation of Airtron production facilities which resulted in diversion of shop personnel to the move.
3. Equipment design and development for handling of large melts required more attention of the project engineer than was estimated.
4. Repeated equipment failures caused the initiation of a program of redesign and upgrading of existing equipment.
5. Failure of new equipment to meet specifications and reliability expectations caused loss of operating time.
6. Equipment redesign and upgrading was much more extensive than had been planned because of the repeated equipment failures.

TABLE I

<u>Item</u>	<u>Goal</u>	<u>Purpose</u>	<u>Current Status</u>	<u>Problems Encountered</u>	<u>Estimated Completion Date</u>
1	Study to determine growth conditions for Cr doped $\text{Al}_2\text{O}_3$ .	To provide crystals for evaluation	Completed 7-62	$\text{Cr}^{3+}$ distribution Pt corrosion, included impurities	Complete
2	Determination of analytical procedures for the detection of Ga in $\text{Al}_2\text{O}_3$ .	Determination of Cr concentration in ruby crystals and flux	Completed 9-62	None	Complete
3	Determination of optimum growth conditions for high quality ruby.	Provide narrow line-width ruby	In progress	Equipment failures Pt corrosion	4-63
4	Determination of analytical procedures for the detection of Ga in $\text{Al}_2\text{O}_3$ .	Determination of Ga concentration in ruby crystals and flux	Completed 11-62	Chemical separation	Complete
5	Study of the growth of Ga doped $\text{Al}_2\text{O}_3$ .	Effect on crystal growth provide crystals for evaluation	Completed 11-62	Effect on crystal habit	Complete
6	Determination of optimum growth conditions for Ga doped $\text{Al}_2\text{O}_3$ .	Provide crystals for evaluation	In progress	Equipment acquisition	4-63
7	Determination of the effect of Ga impurity on the linewidth of ruby.	Determine linewidth broadening	In progress	Equipment acquisition	4-63
8	Comparison of the optical quality of narrow & broad linewidth ruby.	Contract objective	Not started	-----	None

## VI. EXPERIMENTAL

### A. Equipment

Nielsen<sup>1</sup> has shown that in molten salt systems the largest and best crystals grow from the largest melts. With this in mind, an equipment acquisition program was initiated which was intended to provide Airtron with large tube furnaces together with the most advanced and sophisticated control equipment available.

While this equipment was on order, but before it was manufactured, several equipment failures made it evident that existing equipment design was inadequate even for the small systems in use. A program of equipment redesign was urgently needed. It was also obvious that the large furnaces could be improved by incorporating small design modifications.

Problems and solutions used are summarized below:

<u>Problem</u>	<u>Solution</u>
1. Woven metal power strap burned out during run causing partial loss of furnace power. This caused a higher cooling rate than had been programmed.	1. Strap deterioration was caused by flux attack and high temperature encountered, because strap was placed too close to top of furnace. We increased the length of heating elements and used unequal ends. We also used heavy-duty straps. There has been no recurrence of this type of failure.
2. West controller failed due to photo cell lamp burn out. This resulted in rapid cooldown of furnace.	2. Program of preventive maintenance especially before long runs. This failure has not recurred.
3. Top plug broke off. It broke furnace core and crushed Pt crucible.	3. Pour and cure the new plugs strictly according to manufacture's suggested procedure. This failure has not recurred.

Experimental (Continued)

<u>Problem</u>	<u>Solution</u>
4. Elevator-stirrer failure due to movability. Elevator free to move with respect to turntable. Instability of elevator table. Inadequate elevator power. Inadequate stirrer power. Unstable furnace platform.	4. Redesign entire assembly.
5. Inadequate height of legs of furnace which limits placement of sample in furnace.	5. Increase leg height and pedestal length.
6. Inadequate ventilation in furnace room and hood.	6. Install larger hood blower and snorkle arrangement over pouring area.

1. Large System Development

Since the largest and best crystals grow from the largest melts and since the indication is that temperature control is a major factor in crystal quality, a system was planned which would grow crystals from large melts weighing about 100 pounds using the most sophisticated temperature control equipment available.

This system consists of a number of components. These are:

- a. Ten inch i. d. furnace.
- b. Loading-unloading and pouring equipment.
- c. Elevator-stirrer.
- d. Temperature controller.
- e. Exhaust and ventilation equipment.

Experimental (Continued)a. Ten Inch I.D. Furnace

The furnace is an American Electric Furnace Company, mode HTV-1023. It is shown in Figure 1. The ten inch furnace is heated by eight "Globars" wired as four parallel pairs across the two phase 208 volt secondary of a tap transformer. This furnace had some insulation changes from standard to improve the shell temperature. The standard insulation of these vertical tube furnaces called for two 4 1/2 inch courses of fire brick insulation. The inner or hotter of these two was a 2600°F, 1425°C, fire brick. The outer of the two was a 2300°F, 1260°C, fire brick. The insulation was changed to two 3 1/2 inch courses plus an additional 2 inch course of high Q insulation. Aluminum foil was placed around the outside of the high Q insulation which was the 2 inch course. These changes reduced the furnace shell temperature to 70°C at the 1300°C operating temperature. In addition, these insulation changes should improve the operating efficiency of these furnaces.

The furnace has a ten inch inside diameter alumina core. The alumina cores for the furnaces are made of two different materials, Norton RA-98 and RA-139. The RA-98 is the material which has always been used in the past. The RA-139 is a high purity, high density body which is being tested for process improvement and improved furnace life. The core is also being tested both as a one piece unit and a three piece core. The crucible is a platinum can with straight sides and a garbage can type cover. This crucible contains about 100 pounds of flux when fully loaded. This mass



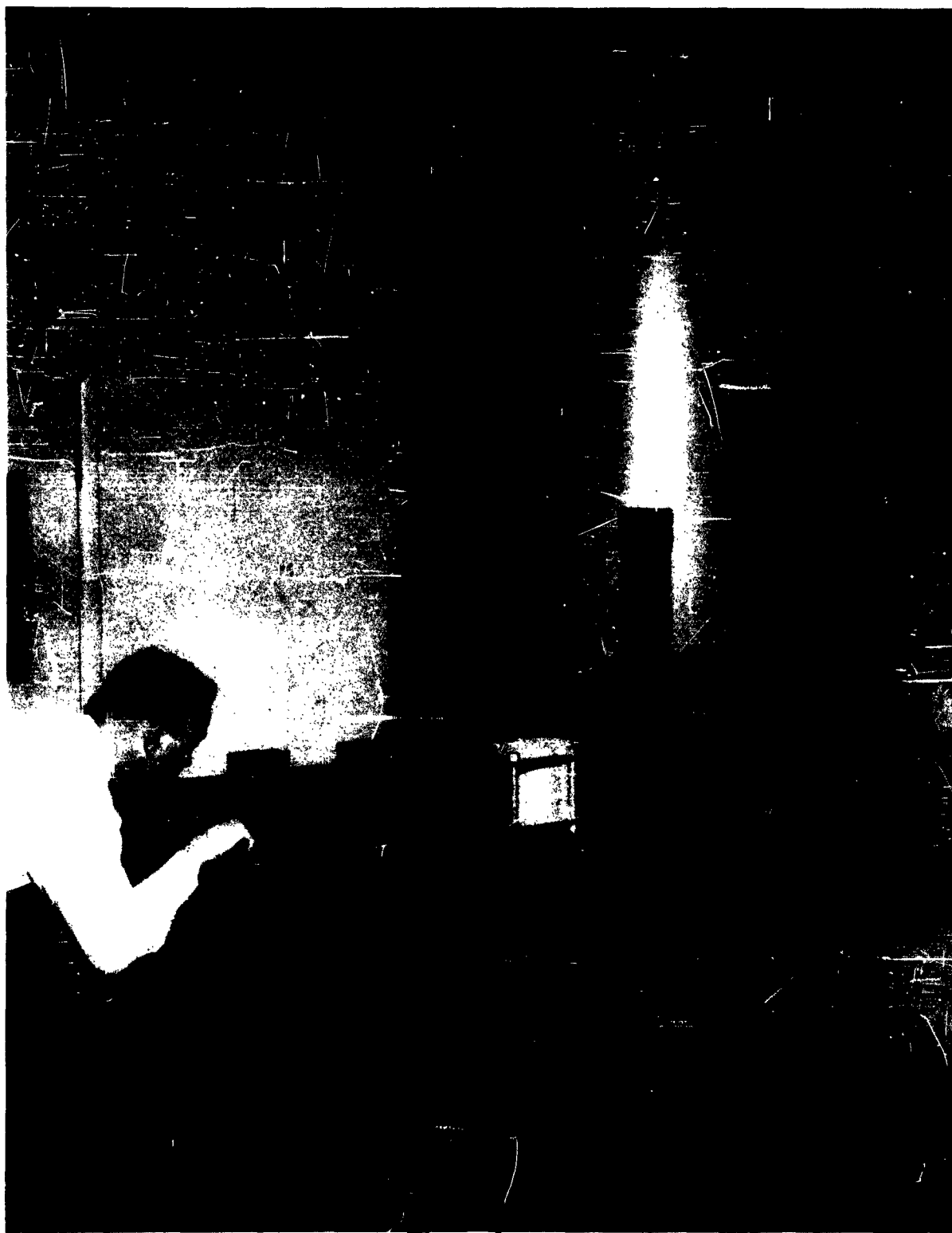


Figure 1  
American Electric Furnace  
Page 13

Experimental (Continued)

of material required the design of special equipment to handle the material and pour flux from the crystals.

Furnace life has always been a problem in molten salt crystal growth work. Furnace failures take place in several ways.

1. The furnace core is attacked by the vapor from the fluxes, especially fluoride vapors.
2. Furnace insulation is attacked by the same fluoride flux vapors.
3. Furnace insulation deteriorates through over-heating.
4. The plugs and pedestals are attacked by either molten lead salts or vapors of these lead salts.

Furnace life is expected to improve when the cores are made of the RA-139 material. This is primarily because the higher density, higher purity product is more resistant to attack by these vapors. As a rule of thumb, it can be said that a material is most likely to deteriorate through chemical attack when it is very close to its melting point. The high purity, high density material is further removed from its melting point, and as a result, is less subject to chemical attack.

b. Loading, Unloading and Pouring Equipment

In the use of the large (10 inch i. d.) furnace, it is necessary to handle large masses of material. This is done while the pedestal is at 1300°C.

Experimental (Continued)

during loading, or the loaded crucible is at 1000°C, before pouring. The total mass of crucible plus charge weighs about 100 pounds.

This mass is impossible to handle by ordinary techniques. For this reason, a device was designed and built especially to do this job. This device must be strong enough to support the weight and pour molten flux. It also must be movable to a precise position with respect to the furnace pedestal. Its manipulation must be simple. The loading or unloading of the furnace must be accomplished in about 30 to 45 seconds after the pedestal has been lowered to its lowest position.

A new device was designed to do this job because nothing was available which would meet these requirements.

A clamshell type of holder was decided upon as the only convenient method of grasping the hot platinum crucible when approached from the front. The steel halves of the shell are lined with a poured insulating refractory. The size is such that it holds with a slight pressure the eight inch crucible; that is, about one-sixteenth of an inch less than eight inches i. d.

The opening of the halves is controlled by a lever attached to a nut on an Acme threaded rod. After one or two tries, this can be manipulated in 5 to 10 seconds to pick up the crucible or place it on the pedestal.

The device is designed to operate on angle iron tracks attached to channels in the floor. Stops will be installed to index position of the pourer.

Experimental (Continued)

Pouring takes place by rotating a handle. Molten material is poured into a sand bath.

The device must be rugged. It is made of several pieces of pipe with extensions, tees, clamps and heavy gauge material. This device appears to work as expected. A photograph is shown in Figure 2.

c. Elevator and Stirrer

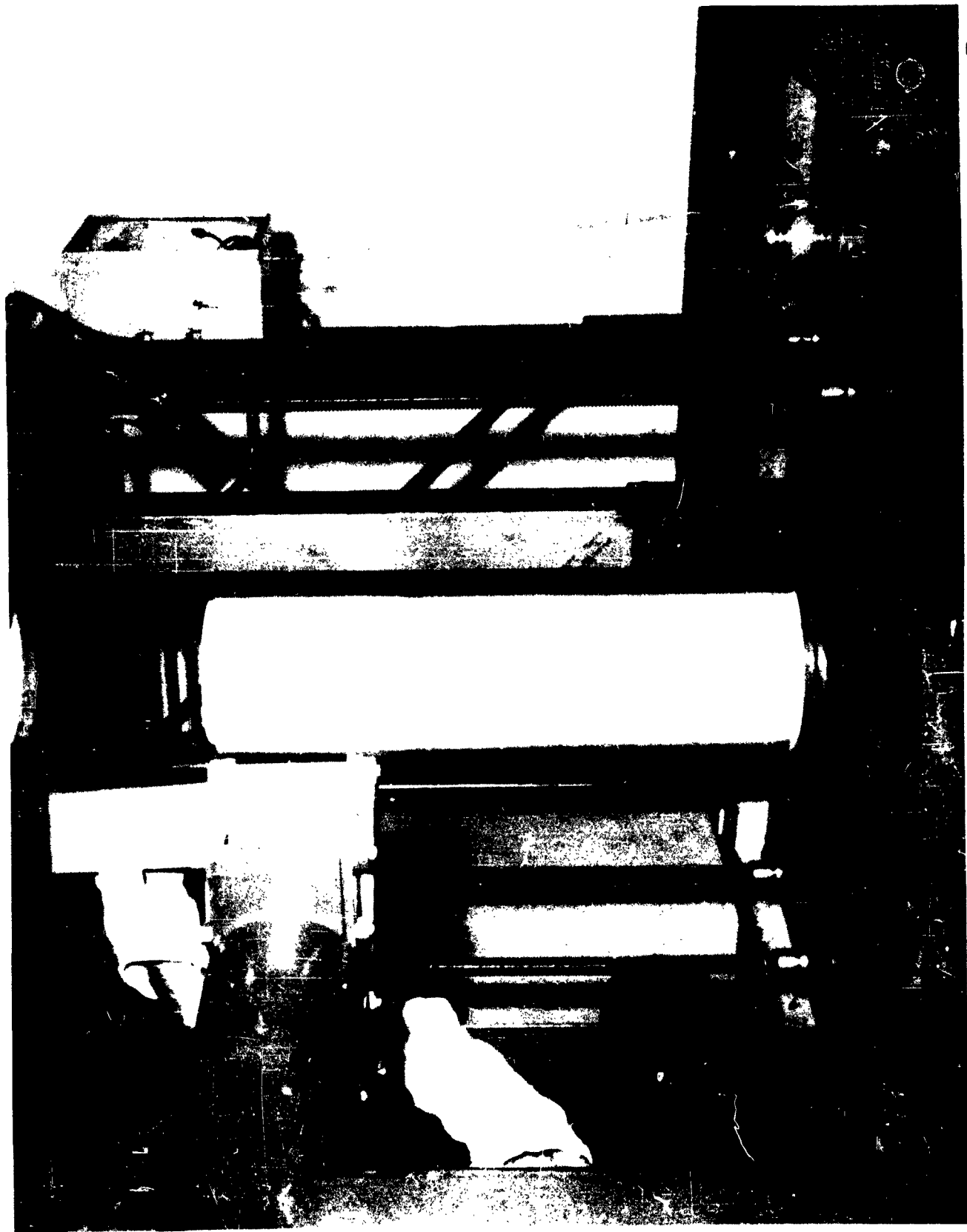
In order to load the furnace, it is necessary to have an elevator. This elevator must be capable of lifting over 200 pounds (pedestal and loaded crucible). In addition, it must be possible to position the load at a number of different levels in the furnace. The movement of the pedestal must be with the axis coincident with the furnace core axis. All movement must be smooth, no jerk or sway can be tolerated when a load of lead fluoride is to be handled at 1000°C or above.

In addition, the apparatus must be provided with a means of measuring the temperature. This is needed to fill a gap in knowledge of melt temperatures and gradients. This is required in the pedestal even while rotating.

These considerations led to an elevator designed to be attached to the furnace. This fixes the physical position of the pedestal relative to the furnace.

Some of the problems encountered were:

1. Elevator drive.



Experimental (Continued)

2. Stirrer drive.
3. Pedestal design.
4. Thermocouple contact.

Possible methods considered for the elevator drive were an electric motor with a mechanical drive or a hydraulic pump. Space ruled out the hydraulic pump. The elevator drive is by a 1/6 h. p. electric motor. A chain drive is used and four Acme threaded screws support the table. A chain drive was selected because four screws must be driven together. The Acme lead screws drive by rotating through bronze nuts attached to the steel table. Another important problem was where to place the drive motor. The possibilities are floor level, attached to the elevator table or at the top of the lead screws. Space demanded that the latter be chosen. The motor is mounted near the bottom of the furnace with the chain running around the outside with idler gears placed to keep the chain clear of the heating elements and under tension.

The elevator motors must, of course, be reversible. This can be accomplished by interchanging two phases of a three phase motor or reversing a capacitor for a single phase motor. The three phase motor is preferable because it gives a positive reversal. It is possible using the single phase motor to reverse the switch without reversing the motor. It is necessary for rotation to stop completely before a single phase motor with two field windings can be reversed.

Experimental (Continued)

The stirrer drive problems included rotation of a load of more than 200 pounds. This was simplified by placing a turntable on a ball bearing raceway. This minimized friction losses. The necessary centering (the rotation must be about an extension of the furnace core axis) was accomplished by placing a drive shaft for the turntable in a bronze bearing on the elevator table. A chain drive was selected for space considerations. Reversal of rotation direction is necessary or the rotating crucible will quickly attain a state of mobile equilibrium. This would reduce stirring action considerably. Motor reversal takes place in a similar manner to that for the elevator drive. There is one major difference. Using the stirrer requires automation of this operation. This is done by using a synchronous motor to drive a cam which operates microswitches to drive the stirrer in one direction for 25 seconds, stop for 5 seconds, drive in the reverse direction for 25 seconds and stop for 5 seconds. These are for a one minute cycle. The microswitches function as a double pole-double throw switch with an off position. This either interchanges a capacitor between two pairs of field windings or interchanges two phases of a three phase motor.

Pedestals and top plugs had to be designed with load support, rotation, temperature measurement and crucible position in a furnace in mind.

Rotation requires that the pedestal be perpendicular to the turntable, have true sides and top surfaces and move concentric with the furnace.

Experimental (Continued)

Temperature measurement is simple in the top plugs with thermocouple wells. These plugs are not rotated. The problem is considerably more difficult when rotation of a pedestal takes place. It can be done, but only by using moving contacts. A set of slip rings with a lava insulator is used. This makes several additional junctions because the thermocouple must be attached to the slip rings. Contact must be made to the slip rings and the contacts attached to the measuring circuit. Each of these contacts is potentially an uncompensated junction. The thermocouple (Pt vs. Pt 13 percent Rh) is soldered to the slip ring. Thermocouple lead wire is attached to the brushes.

The temperature is found to agree with an adjacent thermocouple within 5 degrees, the readability of the recorder, even though potential errors are present. This can be explained by the fact that the temperature is low (25°C or less) and the contacts create pairs of similar opposing junctions.

The plugs and pedestals are poured of a castable refractory (Norton 33HD) with a thermocouple well (high temperature alumina) in place. The molds used are finished to a close tolerance (out of round undetectable with a surface gauge). A steel plate with anchor pins is attached to the pedestal during casting. The steel plate is used with adjustable pins to position the pedestal or the turntable.

The length of the pedestal must be tailored to the furnace. It dictates position of the crucible in the furnace. Pedestal length ideally will be great enough to allow the crucible to be placed at any position in the



Experimental (Continued)

furnace hot zone. It also must be short enough to allow handling of the crucible for loading and unloading the furnace. These two requirements can be mutually exclusive. The size selected to optimize these as well as possible was 33 inches high.

The elevator has been designed and installed. Plugs and pedestals have been delivered and installed.

These pieces of equipment were designed, fabricated and installed under the direction of the project engineer. They are shown in Figure 3.

d. Temperature Controller

The temperature controller for the ten inch furnace is a unit designed and manufactured by Minneapolis-Honeywell. The control system consists of a Beck Program Controller, a Honeywell Temperature Set Point Unit, Deviation Amplifier, Deviation Recorder, Electr-O-Volt 3 mode controller and a Magnetic Amplifier. In this equipment, the temperature set point unit selects a millivolt potential which is compared with the thermocouple output. The two signals, potentiometer and thermocouple, feed the two channels of a deviation amplifier. This unit puts out a signal proportional to the millivolt difference from zero or temperature difference from set point. The set point unit selects the potential by adjusting a ten turn potentiometer. This potentiometer has 537.9 turns per turn or a total of 5379 turns from end to end. Since the scale span is 1600°, the limit of

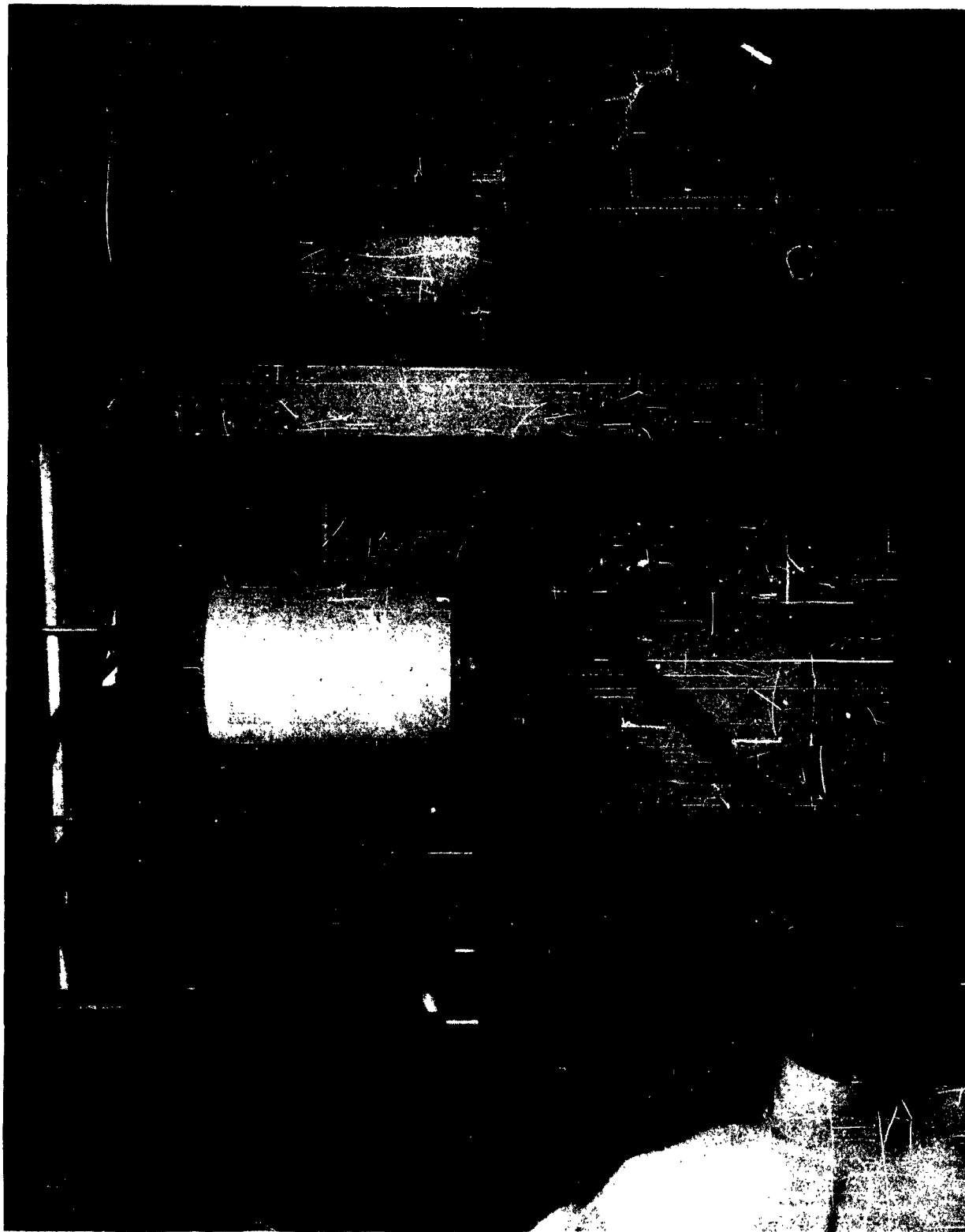


Figure 3 - Elevator - Rotation Assembly  
Airtron, a division of Litton Industries

Experimental (Continued)

resolution of this potentiometer is  $0.3^{\circ}\text{C}$ . This is also the limit of resolution of the equipment. The Deviation Amplifier takes the thermocouple signal and the Set Point signal and retaining the algebraic sign, amplifies the difference and sends an output signal to the Electr-O-Volt. The signal and its magnitude, length of time off set point and rate of approach to the set point all effect the output of this controller. The output signal of the controller goes to the magnetic amplifier which, in turn, controls the degree of saturation of the Saturable Core Reactor. The reactor controls the power input to the furnace.

This control unit operates on a three mode basis. The modes are: Proportional Band (a function of distance from Set Point); Rate (a function of rate of approach to the Set Point); and Reset (a function of the time the temperature has been off set point).

The Beck Program Controller operates a soak from zero to sixty hours. At the end of the soak, a temperature program is initiated. The rate of cooling is controllable from 0.4 to 10 degrees per hour ( $\pm 0.1^{\circ}\text{C}$ ). The cooling rate is controlled by a synchronous motor drive on the ten turn potentiometer. The control panel is shown in Figure 4.

With the various assemblies described above, a system of unusual size, reliability and versatility is now available for the growth of large high-quality crystals.



Figure 4  
Control Panel  
Airtren, a division of Litton Industries  
Page 24

Experimental (Continued)2. Other Furnaces

A Lindberg high-temperature muffle furnace which has a capacity of nine 100 ml Pt crucibles has been installed and four 3 inch furnaces are also available.

The three inch furnaces are similar in design to the ten inch furnace. These furnaces are used for exploratory work related to process improvement. These furnaces use standard 100 milliliter platinum crucibles or 250 milliliter platinum beakers as vessels for crystal growth.

The three inch furnaces are heated by six Globars wired as three series strings of two bars in parallel across the 208 volt line. All are saturable core reactor controlled.

The temperature control units for these three inch furnaces and the Lindberg are all West Instrument Corporation, Model JSBG-3R controllers. These units consist of the temperature controller which is operated on the principle of a beam of light shining on a photocell. The beam is interrupted by a flag as the temperature approaches the set point. The proportional band which drives the magnetic amplifier and the saturable core reactor is determined by the amount of light incident on the photocell. The power input to the furnace is proportional to the programming. By incorporating various timers and interrupters in the circuits, it is possible to control the rate of change of temperature over a range of one-half degree per hour to fifty degrees centigrade per hour. The limit of control at constant

Experimental (Continued)

temperature is about plus or minus two degrees centigrade.

While the temperature control is not nearly as sophisticated on the smaller furnaces, the better control is not really necessary. The very fine temperature control referred to for the 10 inch furnaces is necessary for the growth of large crystals. The smaller 3 inch inside diameter furnaces are used to obtain some of the process information which is applicable to the larger furnaces. Much of this information can be obtained on equipment which is not nearly as precise as the control equipment used on the larger furnaces. The very fine equipment will undoubtedly yield better crystals. The small furnaces are intended more to yield information than crystals. The process improvements are expected to yield more crystals per run as well as higher quality crystals.

The same kind of a statement can be made about the elevators and stirrers for these furnaces. While the requirements are not as great; that is, the elevator is only required to lift a few pounds and the stirrer is required to rotate the same small mass of charge, it was felt that standard elevators and stirrers with as many interchangeable parts as is feasible would allow the maximum utilization of equipment.

The elevator is simply a convenient method of admitting the sample to the furnace. The stirrer serves to reduce the length of time required to soak and dissolve aluminum oxide in the solvent. Stirring, for example, makes the  $Al_2O_3$  go into solution in less than 4 hours at 1280-1300°C

Experimental (Continued)

where it would take many hours at best without stirring. It often is not even possible to dissolve the material at 1300°C without stirring. Sometimes the  $\text{Al}_2\text{O}_3$  sinters into a hard crust on the surface of the melt. Grain growth takes place and the solution rate decreases. Finally, enough solvent is lost through evaporation to separate the crust from the melt and dissolution ceases. Even though the smaller furnaces do not require the elevator and stirrer power, it was decided that standardizing these components would be advantageous. For this reason, all the elevators are as nearly identical as furnace dimensions will permit.

3. Pt Crucibles

The crucibles used in the 3 inch furnaces were 100 ml Pt beakers of 0.020 wall, reinforced rim and bottom and with flat Pt plates as covers which were crimped over the top of the beakers to inhibit vaporization of flux. A 5 1/4 inch x 5 1/4 inch can of 0.030 wall and with a flat but uncrimped lid was used in the 6 inch furnace. (This furnace was not described in detail because it is not planned to use it extensively in the ruby crystal growth program). The crucible planned for use in the 10 inch furnace was a 8 inch x 8 inch Pt can with a garbage can type cover. This crucible had a wall of 0.030 inches with reinforced rim. During the course of this investigation, a new type of cover similar to that ordered with the 8 inch cans was specified for use with the 100 ml crucibles. This cover resulted in substantial reduction of flux evaporation and will be used exclusively in the future. In addition, a 250 ml

Experimental (Continued)

crucible equipped with the garbage can type cover was purchased and tested in the 3 inch furnace. This crucible was chosen because its design more nearly approximated the shape of the larger crucibles in use, and because it permitted more efficient utilization of the 3 inch furnace space, allowing 250 ml of melt to fit into the space previously occupied by a 100 ml crucible. Wall thickness will have to be increased from the 0.012 inches originally supplied to about 0.020 inches. It will then probably replace the 100 ml crucibles in crystal growth runs in the 3 inch furnaces, although the 100 ml crucibles will still find use in the Lindberg muffle furnace.

B. Crystal Growth Data

The general procedure used in growing crystals from molten salt fluxes is as follows:

A given amount of solute and flux is weighed as powders into an appropriate container and heated at a constant temperature until solution is complete. The temperature is then slowly reduced. At some desired temperature, the crucible is removed from the furnace, the molten flux is poured into another container and after cooling, the crystals which remain behind are processed to remove any solidified flux.

Using the method described by Linares<sup>2</sup> crystals of ruby were initially grown in 100 ml Pt crucibles from 200 gms of flux consisting of 120 g  $\text{PbF}_2$  and 80 g  $\text{PbO}$  in which 0.2 mole  $\text{Al}_2\text{O}_3$  was added. Later runs included a scale up in these quantities using the 5 1/4 inch cans as well as



Experimental (Continued)

other modifications in this procedure. Every crystal growth run made is listed in Table II together with the reason the run was made, pertinent details and results obtained.

Certain runs yielded very important and interesting results. Run number 2, for example, succeeded in duplicating the Linares' results, and demonstrated the optical quality and yields obtainable from 100 ml crucibles. Run number 7 was made to determine what kind of improvement could be obtained from a scale up from the 100 ml crucible. The usually dramatic increase in crystal size and quality when large systems are employed was once again demonstrated.

As can be seen from the table, furnace failures plagued early efforts to grow large crystals. These failures, however, still permitted meaningful data to be obtained. Three types of crystals were readily observed in the large batches, and all three forms appeared in the same melts. The three types of crystals observed were:

1. Thin laminated plates, heavily flux included with the easy growth direction perpendicular to the axis.
2. Rhombohedral plates with a ratio of length of the a and c axis of about 2 to 1, and little or no included flux.
3. Rhombohedral chunks, with no included flux, and high optical quality. (See Figure 5).

These crystalline forms also appear in the 100 ml crucibles. Because

TABLE II

Run No.	Units	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	CaO	Type of Run	PbO	PbF <sub>2</sub>	Total	Purpose of Run	Crucible Used	Soak Temp. °C	Recorder	Soak Time Hours	Cooling Rate °C/hr.	Pour Temp. °C	Crystal Yield gms.	% Yield	% Rhombo	% Flux Loss	REMARKS
1.	gms moles m%	20.5 0.2 18.5	1.0 0.007 0.5	0.0 0.0 0.0	Same as Run No. 1	80.0 0.36 34.1	120.0 0.49 46.3	221.5 1.057 99.8	Exploratory Crystal Growth	100 ml crimped cover	1325	1275	16	2.77	960	---	---	---	15.5	Incomplete solution.
2.	Same as Run No. 1								Increased Solution	Same	1375	1275	17	2.29	1080	15	73	---	30	Complete solution. Plates.
3.	Two Times Run No. 1								Test progressing, promoting & stirring in order to increase yield.	Same	---	1280	17.5	2.29	1000	0.0	0.0	---	---	Furnace failure.
4.	Same as Run No. 1								Reduce flux loss by better sealing of cover	Same	1370	1280	17	2.25	980	---	---	---	24	Solidification of melt before flux could be poured.
5.	gms moles m%	20.5 0.2 18.5	1.0 0.007 0.6	0.0 0.0 0.0	Same as Run No. 1	140.0 0.72 66.0	40.0 0.16 14.7	221.5 1.087 99.8	Effect on PbF <sub>2</sub> /PbO ratio on crystal habit	Same	1370	1280	17	2.25	980	---	---	---	---	Incomplete solution.
6.	Same as Run No. 1								Higher temp. for solution	Same	---	1340	17	2.25	1100	21	100	---	48	Large crystal.
7	Thirty times Run No. 1								Scale up 30 times (100 ml crucible), prepared but not pressed.	5 1/4 inch can	1340	1280	24 (stirring)	0.5	800	260	40	52	---	Controller failed but good yield. Pt can rendered useless by deep etching.
8.	gms moles m%	672.5 0.20 20.5	2.5 0.007 0.06	0.0 0.0 0.0	Same as Run No. 1	2400.0 0.96 33.7	3600.0 0.36 45.8	6676.0 1.927 100.1	Reduced Cr content. 10% increase in PbO. 12% increase in PbF <sub>2</sub> to give larger temp. gradient. Higher soak temperature.	5 1/4 inch can	1360	1300	24 (stirring)	0.5	1050	310	4.6	4	17.23	Furnace failure, but satisfactory crystal yield.
9	gms moles m%	20.2 0.1 19.2	0.1 0.007 0.07	0.4 0.002 0.2	Same as Run No. 1	80.0 0.36 34.2	120.0 0.49 46.5	220.7 1.057 100.1	Ga doped Ruby crystals	100 ml crimped cover	1460	1340	17	2.25	1090	---	---	0	39	Flux included plates.
10.	gms moles m%	19.81 0.20 19.1	0.13 0.007 0.07	0.75 0.004 0.4	Same as Run No. 1	80.0 0.36 34.2	120.0 0.49 46.5	220.65 1.0547 100.2	Effect of Ga concentration on ruby crystals	Same	1440	1340	17	2.25	1100	16.2	8.2	0	36	Flux included plates.
11.	gms moles m%	19.37 0.19 18.1	0.1 0.007 0.07	1.88 0.01 0.95	Same as Run No. 1	80.0 0.36 34.2	120.0 0.49 46.5	221.35 1.0507 99.8	Effect of Ga concentration on ruby crystals	Same	1440	1360	17	2.25	1130	---	---	---	38	Flux included plates.
12-1	gms moles m%	22.55 0.22 18.8	0.05 0.003 0.61	0.0 0.003 0.0	Same as Run No. 1	132.0 0.59 50.4	88.0 0.36 30.7	244.60 1.1703 99.9	PbO-PbF <sub>2</sub> ratio on ruby crystal habit	Same	1440	1340	95	5	1060	9.7	43	---	26	Timer failed to switch programmer, heavy flux inclusion.
12-1 (re-run)	gms moles m%	20.90 0.1 19.5	0.1 0.007 0.06	0.0 0.003 0.0	Same as Run No. 1	120.0 0.36 30.8	80.0 0.49 46.8	220.65 1.0507 100.0	Same	Same	1440	1360	17	5	1160	7.2	35	13.9	---	Light flux included crystals. Incomplete solution and flux change.
12-2	gms moles m%	10.07 0.1 10.2	0.05 0.003 0.5	0.0 0.0 0.0	Same as Run No. 1	80.0 0.33 35.9	80.0 0.33 35.9	210.12 0.9703 99.7	Saturation on crystal growth	Same	1440	1340	17	5	---	0	0	0	25	No yield.
12-3	gms moles m%	10.07 0.10 10.5	0.05 0.003 0.5	0.0 0.0 0.0	Same as Run No. 1	80.0 0.36 37.9	120.0 0.49 51.4	210.12 0.9503 99.83	PbO-PbF <sub>2</sub> & Al <sub>2</sub> O <sub>3</sub> concentration	Same	1440	1360	17	5	960	6.1	60	---	49.8	Crystals of white sh. w/ material indicating phase change.
12-4	gms moles m%	20.50 0.10 18.5	0.10 0.007 0.06	0.0 0.0 0.0	Same as Run No. 1	140.0 0.72 64.8	40.00 0.16 14.8	220.60 1.0807 100.16	Same	Same	1440	1365	---	5	---	9	49	50	---	50 percent Rh., 50 white crystals.
12-5	gms moles m%	20.5 0.1 19.4	0.1 0.007 0.06	0.0 0.0 0.0	Same as Run No. 1	160.0 0.64 73.5	20.0 0.11 7.8	220.6 1.0907 99.4	PbO-PbF <sub>2</sub>	100 ml	---	1360	17	5	---	10.3	50	---	---	Possible incomplete solution.
13.	gms moles m%	1035 10.2 18.8	10.35 0.06 0.11	0.0 0.0 0.0	Same as Run No. 1	4570 24.8 44.5	5530 0.96 46.5	11145.35 53.26 100.5	Crystal growth	5 1/4 inch can roasted	1340	1280	24	0.5	1000	365.5	35.4	---	---	Cooling rate increased by accident. Possible incomplete solution but crystal quality excellent.
14.	gms moles m%	820 8.1 19.1	8.20 0.09 0.13	0.0 0.0 0.0	Same as Run No. 1	3200 14.4 34.4	4800 19.5 46.5	8828.20 42.05 100.1	PbO-PbF <sub>2</sub> ratio on large crystal growth	5 1/4 inch can roasted	1340	1280	24	0.5	1000	334.5	41	---	---	Heavily flux included plates.
18-1	gms moles m%	61.5 0.60 19.0	0.61 0.004 0.13	0.0 0.0 0.0	Same as Run No. 1	2400 1.47 34.3	340 1.47 46.6	662.11 3.154 100.0	Starting composition vs. % rh.	250 ml glassware can type cover	1340	1280	12	3.80	Solidified	15	25	Small amt.	6.5	some crystal growth.
18-2	gms moles m%	61.50 0.60 19.0	0.61 0.004 0.13	0.0 0.0 0.0	Same as Run No. 1	100 1.22 42.5	140 1.22 38.0	662.11 3.154 100.2	Same	Same	Same	Same	Same	Same	Same	---	---	---	3.8	Incomplete solution.
18-3	gms moles m%	61.50 0.60 18.4	0.61 0.004 0.12	0.0 0.0 0.0	Same as Run No. 1	140 1.42 45.9	240 1.00 30.7	662.11 3.224 100.1	Same	Same	Same	Same	Same	Same	Same	---	---	---	7.3	Same
21. (1-4)	gms moles m%	20.50 0.20 19.2	0.20 0.001 0.1	0.0 0.0 0.0	Same as Run No. 1	80.0 0.36 34.3	120.0 0.45 46.6	221.70 1.093 100.2	Isothermal growth	100 ml	1290	1280	12	50	970 840 795	---	---	---	---	Incomplete solution in all cases but rh. seed dissolved in else.



Figure 5 - Rhombohedral Chunks of Ruby

Experimental (Continued)

of the high optical quality and freedom from flux inclusions in the rhombohedral forms, it is desirable to find those conditions which favor this form of growth. Linares reports<sup>3</sup> that the  $\text{PbO-PbF}_2$  ratio in the starting composition affects the percent of rhombohedral phase in the yield. The results of run number 13 appear to indicate a correlation between these two factors, but a severe decrease in solubility of  $\text{Al}_2\text{O}_3$  in melts containing small amounts of  $\text{PbF}_2$  indicates that ratios much below 40 percent may not be practical.

Ga was incorporated into ruby in runs, number 9, 10, and 11. The Ga additions appear to increase the platey habit of the crystals somewhat but this was not definitely established.

One major problem encountered in the growth of ruby crystals from  $\text{PbO-PbF}_2$  fluxes is the rapid corrosion of the platinum crucible. Following each run using the 5 1/4 inch can for example, the can was so badly etched it had to be returned as scrap and a new can purchased. This happened in spite of the fact that furnace failures cut the time the run was scheduled to be in the furnace by about 50 percent. Since platinum is susceptible to attack by lead, some reaction must occur which reduces  $\text{PbO}$  to lead during the run, and this lead is not oxidized to  $\text{PbO}$  before it can do any damage. While we do not know as yet what the reaction is, several possible solutions to the problem exist. These are:

1. Increase the purity of the components.
2. Use higher oxides of lead in the flux.

Experimental (Continued)

3. Rotate the crucible during the cooling cycle as well as during the soak.

4. Shorten the run by reducing the soak period, reduce the soak temperature, increase the cooling rate, or all three.

C. Phase Equilibria

The method used to study phase equilibria in the system was to heat several 100 ml crucibles in the Lindberg furnace, and quench the reaction at specified intervals by removing the crucible from the furnace and pouring off the molten flux. While some delay is involved in removing the tightly fitted garbage can covers from the hot crucibles, it is believed that fairly accurate results can be obtained using this technique. All the phase equilibria runs are summarized in Table III, together with the reason for the run, the starting composition and pertinent remarks.

It can be seen from Table III that 0.2 m  $\text{Al}_2\text{O}_3$  in 200 gms of 60 wt. percent  $\text{PbF}_2$  and 40 wt. percent  $\text{PbO}$  results in substantial undersaturation of the melt since in number 17, only 14, 26 and 30 percent yields of  $\text{Al}_2\text{O}_3$  were obtained at temperatures of 1010, 990, and 960 when vaporization losses were inhibited. The crystals were all thin plates in these runs with no rhombohedra present and apparently low Cr content. It is apparent also that all future solubility work must be carried out with stirring and a better idea of the effect of saturation on the crystal habit and Cr distribution in the crystal must be obtained.

TABLE III

Run No.	Type of Run					Totals	Purpose	Soak Temp. °C		Cooling Rate °C Hrs.	Quench Temp. °C	Crystal Yield	% Rhombo	Wt. Loss	REMARKS			
	Units	Al <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Ga <sub>2</sub> O <sub>3</sub>	PbO			PbF <sub>4</sub>	gms			%	gms	%				
15-1	gms	20.5	0.20	0.0	80.0	120.0	Quench temp. vs % yield from 80 percent PbF <sub>4</sub>	---	1320	16	5*	1030	9	43	small amt.	43	21	
	moles	0.20	0.013	0.0	0.36	0.49												
	m %	18.9	1.2	0.0	34.0	46.3												
15-2	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	16	5	1020	12.15	59	2	75	37	
15-3	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	16	5	1000	11.5	55	0.0	49	24	
16-1	Same as Run No. 15-1						Same as Run No. 15-1	Same	1290	12	4	1240	0.0	0.0	0.0	27.15	13	
16-2	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	----	---	---	---	---	--	Muffle failed in Lindberg
16-3	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	----	---	---	---	---	--	Muffle failed in Lindberg
17-1	Same as Run No. 15-1						Same as Run No. 15-1		1285	10	5	1155	0.0	0.0	0.0	8.95	4.5	
17-2	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	1135	0.0	0.0	0.0	10.00	5.0	
17-3	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	1110	0.0	0.0	0.0	6.00	3.0	
17-4	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	1010	3.0	14	0.0	4.85	2.0	
17-5	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	990	5.50	26	0.0	5.85	2.9	
17-6	Same as Run No. 15-1						Same as Run No. 15-1	Same	Same	Same	Same	960	6.28	30	0.0	10.55	5.3	
18	See Table II																	Incomplete solution
20-1	gms	24.60	0.25	0.0	80.0	120	Al <sub>2</sub> O <sub>3</sub> solubility as function of initial PbO PbF <sub>2</sub> ratio	---	1280	12	5	1000	0.0					Incomplete solution
20-2	gms	26.65	0.27	0.0	80.0	120	Same as Run No. 20-1	---	1280	12	5	1000						Incomplete solution
20-3	gms	24.60	0.25	0.0	120	80	Same as Run No. 20-1	---	1280	12	5	1000						Incomplete solution
20-4	gms	26.65	0.27	0.0	120	80	Same as Run No. 20-1	---	1280	12	5	1000						Incomplete solution
20-5	gms	24.60	0.25	0.0	160	40	Same as Run No. 20-1	---	1280	12	5	1000						Incomplete solution
20-6	gms	26.65	0.27	0.0	160	40	Same as Run No. 20-1	---	1280	12	5	1000						Incomplete solution

Experimental (Continued)D. Chemical Analysis

The development of accurate and reproducible analytical methods was a major objective during the report period. The detection of gallium in the presence of aluminum was given special attention.

The analytical procedure used was as follows:

A finely powdered sample is fused with potassium pyrosulfate and the fusion extracted with dilute sulfuric acid. The precipitated lead sulfate after washing is filtered, dried, weighed, and from its weight the lead in the original sample is calculated. Gallium is precipitated from the filtrate using Cupferron. The precipitate is filtered, washed and ashed, then dissolved in nitric acid, take up in dilute sulfuric acid and the gallium-Cupferron complex again precipitated. When ashed again to give gallium oxide, it is weighed and the weight in the original sample calculated. After making the filtrate alkaline with sodium hydroxide and boiling with sodium peroxide, chromium is determined by titration with standard sodium thiosulfate solution and the weight of chromic oxide in the original sample calculated. Aluminum is determined in the filtrate by precipitating the hydroxide with ammonium hydroxide, dissolving in hydrochloric acid and reprecipitating as aluminum phosphate which after ashing allows the weight of aluminum oxide in the original sample to be calculated.

A second sample of the original material is fused with sodium silicate, sodium carbonate, and potassium carbonate. The fusion is taken

Experimental (Continued)

up in water, made acid with hydrochloric acid, perchloric acid is added, and fluoxocilic acid is steam distilled off. The distillate is titrated with standard thorium nitrate solution from which the weight of fluoride in the original sample is calculated. From this result and the known percent of lead in the original sample, the percent of lead fluoride and lead oxide can be calculated.

The results of the chemical analysis are shown in Table IV.

The major problem in the analysis of ruby crystal appears to be sample preparation. Before any analytical work can be started, only a single phase must be present. Two techniques can be used to remove included lead salts from ruby crystals. One is to crush and powder a large sample, and repeatedly extract included lead flux with dilute nitric and acetic acid, testing the extract for lead until no more appears.

Another method is to fire the powdered sample in a chlorine gas stream in a quartz tube at 1000°C for 8 hours. This treatment should remove PbO as a chloride, and PbF<sub>2</sub> would also be volatilized. The remaining sample should then be analyzed by the method described above. Al<sub>2</sub>O<sub>3</sub> should also be analyzed, not simply calculated by difference.

In the analysis of the flux, one problem could be the formation of AlF<sub>3</sub> which during the sodium silicate fusion forms an insoluble salt, perhaps NaAlF<sub>6</sub> (cryolite). In order to eliminate this possibility, and the possibility



TABLE IV  
ANALYZED FOR

Run No.	Sample	Unit	Al <sub>2</sub> O <sub>3</sub>			Fe <sub>2</sub> O <sub>3</sub>			CaO			SiO <sub>2</sub>			Total		
			wt. %	g/g	g/g	wt. %	g/g	g/g	wt. %	g/g	g/g	wt. %	g/g	g/g	wt. %	g/g	g/g
7	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
8	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
9	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
12	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
13	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
14	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
15	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
16	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
17	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
18	1-4	5	61.5	1.5	0.0	10.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
			1.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

1. In crystals that was reported as Fe and calculated as FeO. In all cases, other than this one, Al<sub>2</sub>O<sub>3</sub> in crystals was calculated by difference, other than this one, Al<sub>2</sub>O<sub>3</sub> in crystals was calculated by difference. FeO and Fe were analyzed and calculated as FeO, with FeO determined by difference.

1. Ca concentration was uncertain and it was ignored in calculations.

Fe = 0.46 wt. percent  
FeO = 0.36 wt. percent

Experimental (Continued)

of an additional reaction between  $\text{Al}_2\text{O}_3$  and  $\text{PbF}_2$  during fusion, the  $\text{PbO}$ ,  $\text{PbF}_2$  and  $\text{AlF}_3$  in the flux should be separated from the  $\text{Al}_2\text{O}_3$ ,  $\text{Ga}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$ .

Samples of  $\text{Al}_2\text{O}_3$ ,  $\text{PbO}$ , and  $\text{PbF}_2$  from various sources were analyzed spectroscopically to determine the level of impurities in these chemicals. Table V is a list of all the chemical so analyzed.

These results show that in  $\text{Al}_2\text{O}_3$ , a substantial improvement in purity can be obtained by using either AIAG or Linde B high purity  $\text{Al}_2\text{O}_3$ . There is, however, a price increase of about 100 times over the Fisher material. Therefore, for exploratory work  $\text{Al}_2\text{O}_3$  supplied by Fisher, or Baker and Adamson, will be used. High purity AIAG alumina has been ordered, for use only when high quality crystals are required.

Fisher  $\text{PbF}_2$  and  $\text{PbO}$  is quite pure, and while Airtron has been able to produce a somewhat purer product, the time and expense involved in producing these chemicals in the quantities required would be enormous. Therefore,  $\text{PbF}_2$  and  $\text{PbO}$  were ordered from Fisher Scientific Co.

$\text{Ga}_2\text{O}_3$  used is a better than 99.99 percent product purchased from AIAG.  $\text{Cr}_2\text{O}_3$  used is reagent grade material supplied by Fisher Scientific Co.

E. Physical Analysis

**TABLE V****Units in Parts Per Million****SAMPLE:  $Al_2O_3$** 

<b>Analyzed by:</b>	<b>Ledoux</b>	<b>Litton</b>	<b>Ledoux</b>	<b>AIAG</b>	<b>Ledoux</b>	<b>Litton</b>	<b>Litton</b>
<b>Source:</b>	<b>Linde B</b>	<b>Linde B</b>	<b>AIAG</b>	<b>AIAG</b>	<b>Republic Foil</b>	<b>B &amp; A</b>	<b>Fisher</b>
Gallium	20	1	n. d. < 10	10	n. d. < 10	20	10
Silver	3	--	n. d. < 1	--	1	--	--
Calcium	10	n. d.	10	--	100	10	10
Copper	2	--	4	10-100	20	--	--
Iron	20	10	20	10	150	300	200
Lithium	n. d. < 2	--	n. d. < 2	--	n. d. < 2	--	--
Magnesium	1	10	5	--	70	60	30
Sodium	50	n. d.	20	--	50	550	500
Nickel	n. d. < 10	--	n. d. < 10	--	10	--	--
Lead	150	10	20	1	20	n. d.	n. d.
Silicon	70	10	30	10	300	550	170
Potassium	30	--	10	--	20	--	--
Tantalum	--	--	--	1	---	--	--
Zinc	--	--	--	10	---	--	--
Barium	--	--	--	0.5	---	--	--
Manganese	--	n. d.	--	10	---	5	5
Boron	--	--	--	10	---	--	--
Chromium	--	--	--	0.1	---	--	--

**TABLE V (Continued)****Units in Parts Per Million****Analyzed by Ledoux****SAMPLE: PbO**

<b>Source:</b>	<b><u>B &amp; A</u></b>	<b><u>Fisher</u></b>	<b><u>Airtron</u></b>
Silver	1	4	n. d. < 1
Aluminum	5	5	5
Barium	n. d. < 2	5	n. d. < 2
Bismuth	n. d. < 5	50	15
Calcium	20	n. d. < 10	60
Copper	1	3	1
Iron	20	7	4
Lithium	5	2	3
Magnesium	1	1	1
Sodium	20	20	20
Silicon	40	20	5
Potassium	10	10	10

**SAMPLE: PbF<sub>2</sub>**

Silver	10	1	n. d. < 1
Aluminum	3	10	1
Barium	n. d. < 2	5	n. d. < 2
Bismuth	100	n. d. < 5	n. d. < 5
Calcium	20	n. d. < 10	n. d. < 10
Copper	1	n. d. < 1	n. d. < 1
Iron	70	7	n. d. < 3
Lithium	5	3	2
Magnesium	3	1	n. d. < 1
Sodium	20	20	10
Silicon	5	5	5
Potassium	n. d. < 10	10	n. d. < 10

## Experimental (Continued)

### 1. Linewidth Measurements

In order to study the fluorescent spectra of crystals at low temperatures, the experimental apparatus shown in Figure 6 was designed by the Electron Tube Division of Litton Industries. The light source consisted of four General Electric 150 watt focused projection bulbs. The bulbs have a dichroic focusing mirror that passes infrared heating rays and reflects and focuses visible and ultraviolet radiation. The projection bulbs are immersed in a saturated aqueous copper sulfate bath. This bath acts as a filter, and has the transmission spectra shown in Figure 7. The focusing of the dichroic mirror is dispersed at the liquid-glass interface. The addition of lucite rods as cylindrical lenses helps to restore the focus in the horizontal plane.

The crystal, immersed in liquid nitrogen is held in a quartz dewar flask which acts as a window for the fluorescent output. The fluorescent light is then directed into the Jarrell-Ash spectrograph.

This equipment is being calibrated and results on linewidth will be available shortly. Samples are now in the hands of Mr. Story of the Electron Tube Division.

### 2. Optical Measurements

Crystals were observed under magnification for flaws and inclusions. The rhombohedral chunks were the most perfect showing no observable defects even under the highest magnification. Some small areas

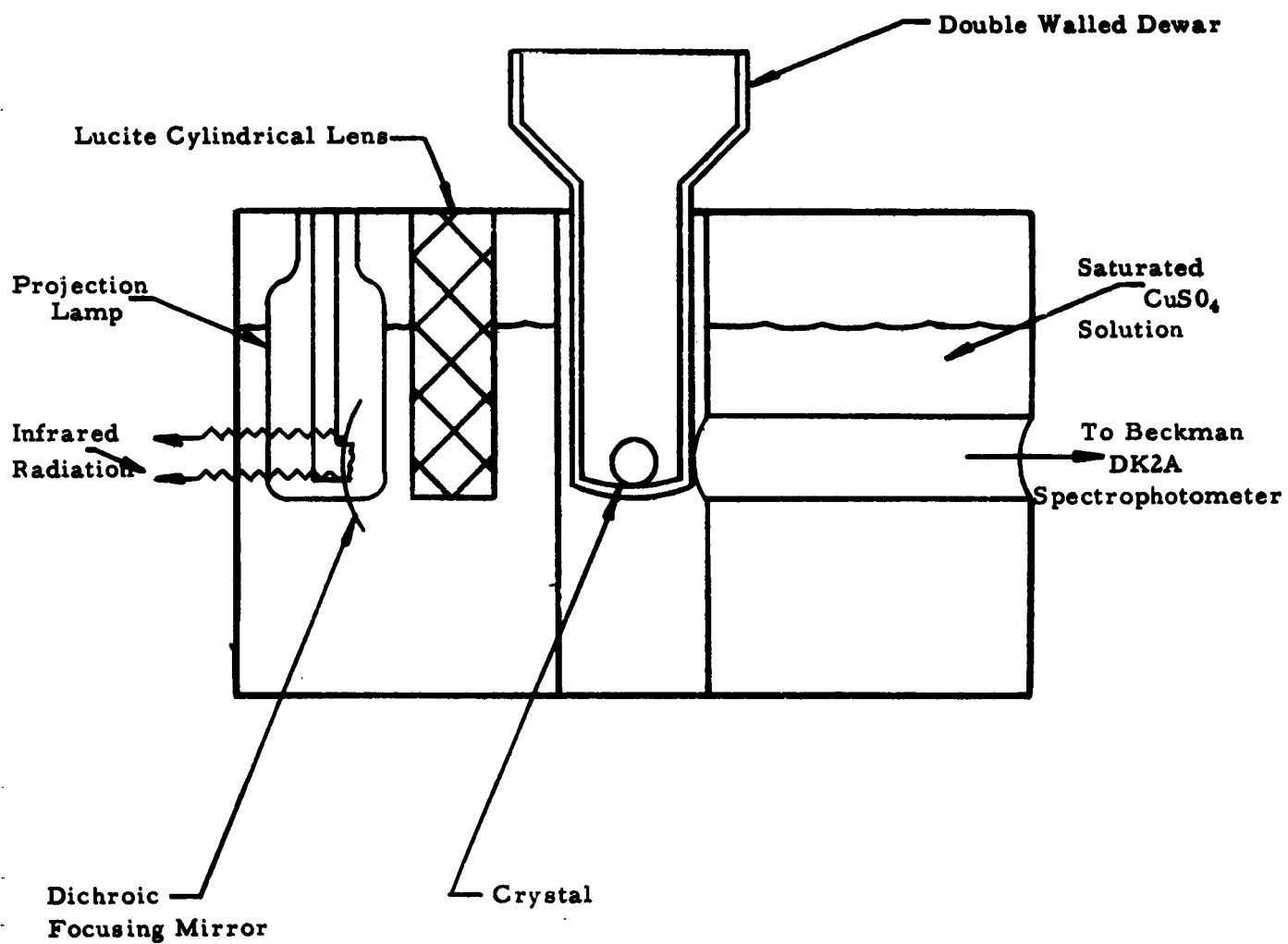


Figure 6

Apparatus for Linewidth Measurements

Airtron, a division of Litton Industries

Sample \_\_\_\_\_  
 a. 1.5/1.5  
 b. \_\_\_\_\_  
 c. \_\_\_\_\_  
 d. \_\_\_\_\_  
 Solvent \_\_\_\_\_  
 Path cm \_\_\_\_\_  
 Slit Width \_\_\_\_\_  
 Sens \_\_\_\_\_  
 Time Const \_\_\_\_\_  
 Scanning Speed \_\_\_\_\_  
 Source \_\_\_\_\_  
 T \_\_\_\_\_ W \_\_\_\_\_  
 Other \_\_\_\_\_  
 Detector \_\_\_\_\_  
 R \_\_\_\_\_ P \_\_\_\_\_ S \_\_\_\_\_  
 Other \_\_\_\_\_  
 Spectra \_\_\_\_\_  
 Trans \_\_\_\_\_  
 Abs \_\_\_\_\_  
 Refl \_\_\_\_\_  
 Fluor \_\_\_\_\_  
 Date \_\_\_\_\_  
 Run By \_\_\_\_\_

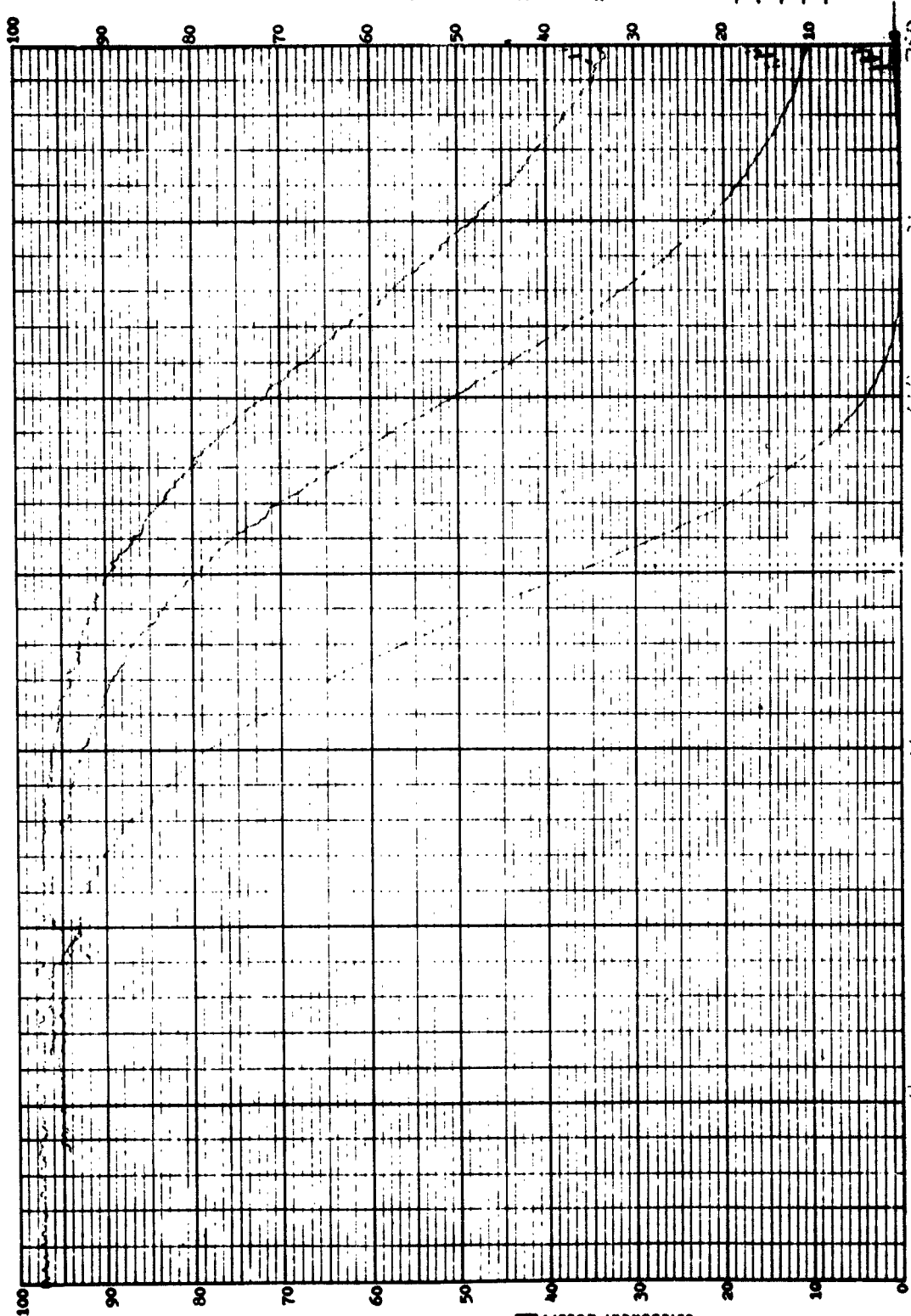


Figure 7b - Transmission Curve of CuSO<sub>4</sub>

Experimental (Continued)

of plates were clear and of high optical quality, but large areas almost always showed some flux inclusions as filaments or bubbles when closely examined. Examination under crossed polaroids revealed some strain in all crystals, but some were obviously less strained than others. No attempt was made to relieve strain by subsequent annealing. Airtron has borrowed from the Linde Co. for comparison with flux grown crystals the best low strain high quality disk shaped flame fusion ruby available.

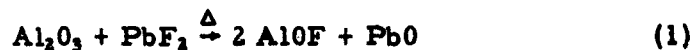
A device for measuring light scattering has been designed and used by R. L. Barns and D. L. Herriot of the Bell Telephone Laboratories and seems to meet our requirements for a light scattering measurements. It will be built and modified if necessary at Airtron for light scattering studies.



## VII. DISCUSSION OF RESULTS

A possible mechanism for the growth of ruby from solution can be made from an analysis of the data presented above.

Consider the reaction:



For every mole of  $\text{Al}_2\text{O}_3$  and  $\text{PbF}_2$  present, two moles of  $\text{AlOF}$  and one mole of  $\text{PbO}$  is formed. As heat is removed from the system, the reaction can reverse or this reaction can occur:



Let us consider run number 13, Table II. In this run, large flux free crystals formed, but there was some indication of undissolved  $\text{Al}_2\text{O}_3$ . From Table II, it can be seen that the starting composition of number 13 was as follows:

$\text{PbO} = 25$  moles

$\text{PbF}_2 = 18$  moles

$\text{Al}_2\text{O}_3 = 10$  moles

If (1) represents the reaction that takes place, the composition of number 13 at  $1300^\circ\text{C}$  looked like this:

$\text{PbO} = 35$  moles

$\text{PbF}_2 = 8$  moles

$\text{Al}_2\text{O}_3 = 0$  moles

$\text{AlOF} = 20$  moles

Now, if this was close to the ideal composition, and if some  $\text{Al}_2\text{O}_3$

Discussion of Results (Continued)

remained undissolved, and if solubility of  $\text{Al}_2\text{O}_3$  is as strongly dependent on  $\text{PbF}_2$  as (1) suggests, then a small additional amount of  $\text{PbF}_2$  should have been added. The ratio of  $\text{PbO}$  to  $\text{PbF}_2$  would then have been very close to 3 to 1. If we assume that this ratio represents the ideal ratio of  $\text{PbO}$  to  $\text{PbF}_2$ , then

$$x + a = 3(y-a) \quad (3)$$

Where

$x$  = moles of  $\text{PbO}$

$y$  = moles of  $\text{PbF}_2$

$a$  = moles of  $\text{Al}_2\text{O}_3$

represents an equation which gives the ideal starting composition for all values of  $y$  such that  $3(y-a) \geq a$ .

Let us examine runs numbers 1, 12, and 13 in terms of equation (3).

Run No.	Orig. Comp. in moles		Composition at 1300°C	Ideal Comp. at 1300°C	Starting Comp. from (1)	$\Delta\text{PbF}_2$ Conc. from orig.
1	$\text{PbO}$	36	56	56	36	-10.3
	$\text{PbF}_2$	49	29	18.7	38.7	
	$\text{Al}_2\text{O}_3$	20	0	0	20	
12	$\text{PbO}$	59	81	81	59	+13.0
	$\text{PbF}_2$	36	14	27	49	
	$\text{Al}_2\text{O}_3$	22	0	0	22	
13	$\text{PbO}$	25	35	35	25	+3.5
	$\text{PbF}_2$	18	8	11.5	21.5	
	$\text{Al}_2\text{O}_3$	10	0	0	10	

From Table III, it appears that the composition used in number 1 was

Discussion of Results (Continued)

undersaturated, (see number 17), while in number 12 and 13, (Table II),  $\text{Al}_2\text{O}_3$  was incompletely dissolved.

If the above analysis is correct, a considerable range of  $\text{PbO-PbF}_2$  concentrations exist for the crystallization of ruby. The role of  $\text{PbO}$ , however, remains obscure. Its importance is obvious from the fact that for some reason three moles of  $\text{PbO}$  must be present for each mole of  $\text{PbF}_2$  in the melt. Perhaps this ratio has something to do with the stability of  $\text{AlOF}$  in the hot solution. It cannot be stated at this time whether all ratios of  $\text{PbO-PbF}_2$  will yield the same quality or type of crystals.

### VIII. PROGRAM FOR NEXT PERIOD

The implications of (1), (2), and (3) above will be explored. Formula (1) implies that only  $\text{PbF}_2$  is important in the solubility of  $\text{Al}_2\text{O}_3$ . Therefore, from (3), concentrations of  $\text{PbF}_2$  from 100 percent to  $3(y-a) = a$  should dissolve  $\text{Al}_2\text{O}_3$  in accordance with (1). As  $3(y-a)$  becomes smaller than  $a$ , some reaction other than (1) and (2) should come into play.  $\text{Al}_2\text{O}_3$  might now dissolve in, and recrystallize from,  $\text{PbO}$ .

These possibilities will be explored in the following way: Using compositions from equation (3), we plan to determine solubility and crystal growth from fluxes consisting of 100 percent  $\text{PbF}_2$ , 100 percent  $\text{PbO}$  and from fluxes where  $3(y-a) = a$ . Then, we plan to plot any deviation from the solubility predicted by (3) and attempt to explain the discrepancy.

We also want to:

1. Determine the effect of temperature gradient on crystal growth.
2. Reduce the attack on the Pt cans by rotation and faster cooling rates and determine the effect of these changes on crystal quality.
3. Continue phase equilibria and growth kinetics studies.
4. Construct apparatus for measuring light scattering in ruby.
5. Determine the effect of Ga concentration on the linewidth of ruby.

**IX. SUMMARY AND CONCLUSION**

Growth of large ruby crystals from molten salt solutions has been achieved and the design of a system to handle large masses of molten materials has been described. A mechanism for the growth of ruby from  $\text{PbO-PbF}_2$  fluxes has been proposed.

Ga has been incorporated into ruby using similar techniques and evaluation of these crystals is underway.

X. REFERENCES

1. J. W. Nielsen, private communication.
2. R. C. Linares, J. App. Phys., 33, 5, 1747-1749, May 1962.
3. Ibid.